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State-to-state Reactive and Collisional Dynamics
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13. ABSTRACT (Maximum 200 words)

The AFOSR/AASERT research efforts over the past three years (12/93-9/96) have achieved the following goals. 1) We have now completed state-to-state scattering measurements for CH₄, H₂O and HF with rare gas (Ar, Ne and He) collision partners, based on direct infrared absorption in crossed molecular beams. 2) Hot atom state-to-state scattering of Cl with HCl has been studied using high resolution Dopplerimetric techniques to obtain both differential and total state-to-state cross sections. 3) The theoretical basis for extracting O₂(¹Δ) radiative rates from direct absorption studies has been reanalyzed, and which corrects a nearly 2 fold error between inferred and literature values for the O₂(¹Δ) - O₂(³Σ) radiative lifetime. 4) Rotational alignment of CO₂ by collisions with He in supersonic beams have been studied. 5) Nascent quantum state distributions for CO₂ subliming from thin molecular films have been measured. 6) Slit discharge techniques for generating high radical and molecular ion densities have been developed for hyperthermal beam sources of reactive species.

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AFOSR/AASERT Final Report

Title: State-to-state reactive and collisional dynamics of atmospheric species

Principal Investigator: David J. Nesbitt

Institution: University of Colorado

Inclusive Dates: 12/93-9/96

Contract/Grant number: F49620-93-0444/AFOSR-93-NC-231

Senior Research Personnel: David J. Nesbitt

Junior Research Personnel: William Chapman
Brad Blackmon
Miles Weida
Axel Kulcke (DFG Fellowship)
Scott Davis
David Anderson

Objectives:

The objectives of this research effort are to develop and exploit novel high resolution IR laser based methods for study of state-to-state reactive and inelastic collision dynamics in molecular species relevant to characterizing atmospheric airglow phenomena.

Summary of research accomplishments under current funding period (1993-1996):

Productivity during the current funding period has been high; over the last three years, 13 papers from our group have been accepted, in press or published on AFOSR supported projects. These manuscripts are listed in Sec. IV at the end of this proposal, and results summarized below.

A. State-resolved integral/differential scattering via IR laser absorption in crossed jets

The major research focus of this granting period has been towards developing and exploiting novel IR laser methods for quantum state-to-state collisional energy transfer of atmospheric species (CH_4 , H_2O , CO_2 , HX) in crossed supersonic jets. The basic approach consists of i) supersonic cooling of IR "absorber" molecules into the lowest rotational quantum state, ii) inelastically scattering with a "collider" species (typically Ar, Ne or He) in the low density region

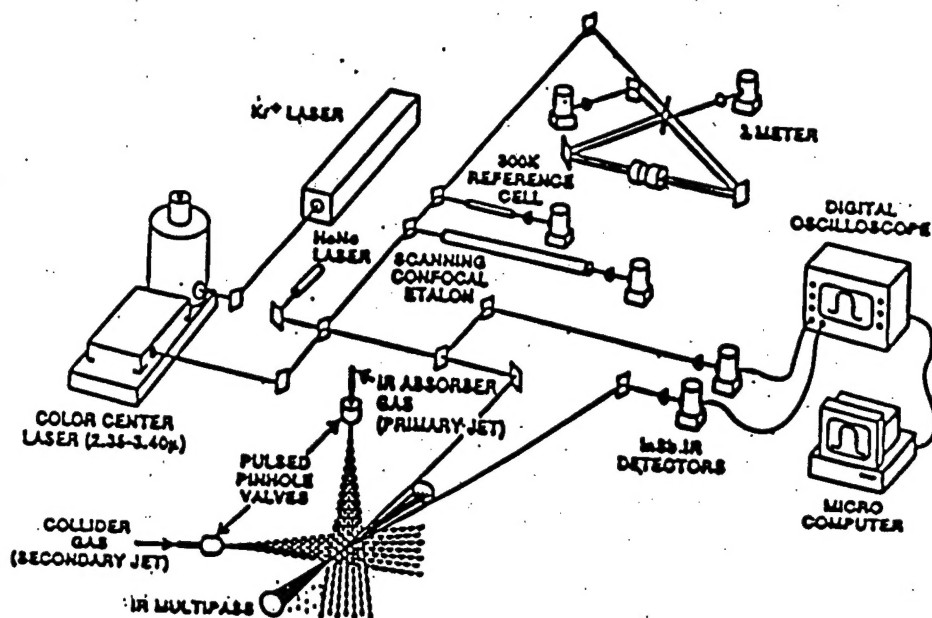


Fig 1. Schematic of the state-to-state crossed jet apparatus

≈ 10 cm from both nozzles, and iii) probing quantum state and velocity distributions via direct absorption of a single mode IR laser (see Fig 1). Velocity distributions are measured directly by optical time of flight, which permits the Newton diagram for the scattering event to be constructed quantitatively (Fig. 2). Different final states on the Newton diagram are accessed by tuning to different rovibrational transitions; plots of integrated absorbance vs. collider density are then used to extract integral cross sections for state-to-state scattering.

The IR approach provides several important advantages over other previous techniques for inelastic scattering. First of all, the $\Delta\nu \leq 0.0001 \text{ cm}^{-1}$ resolution of the Doppler limited probe laser permits a 10^4 fold improvement in state resolution over TOF methods ($\Delta\nu \approx 10\text{-}100 \text{ cm}^{-1}$), and therefore makes larger molecular systems feasible. Secondly, IR absorption is "general", i.e.

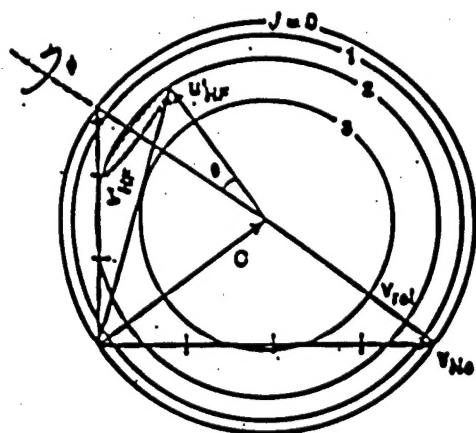


Fig. 2. Newton velocity diagram for Ne + HF scattering

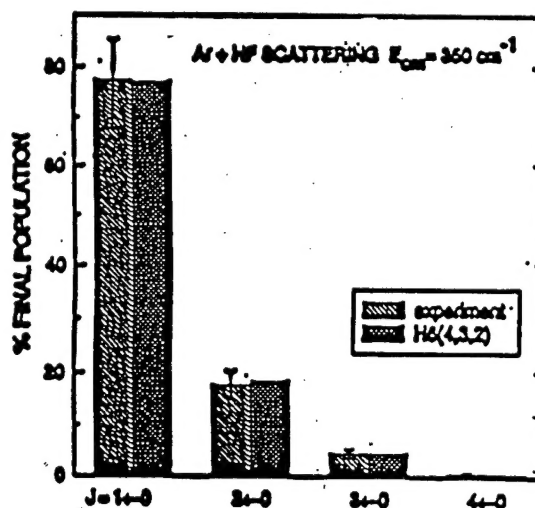


Fig. 3. Ar + HF(J=0) scattering: theory and experiment

permits probing of a wide class of *closed shell* atmospheric species (e.g. CH_4 , H_2O , CO_2) molecules inaccessible to LIF or REMPI. (In this regard, however, it is worth noting the very beautiful work by Wodtke and Meyer on state-to-state reactive/inelastic scattering of O_2 and NH_3 using SEP and REMPI methods as well as the many excellent LIF/REMPI studies of scattering in *open shell* systems by Dagdigian, Liu, Crosley, Andresen, Houston, Zare, Gentry and others.) Thirdly, the direct absorption methods yield absolute (column integrated) densities, which allow state-to-state integral cross sections to be determined absolutely. Finally, these data can be analyzed with "exact" full close coupled QM scattering methods, which facilitate rigorous comparison between experiment and theory for trial potential energy surfaces. As an example, sample data for $\text{Ar} + \text{HF}$ scattering at $E_{\text{com}} = 350 \text{ cm}^{-1}$ is shown in Fig. 2; the agreement between theory and experiment for such a "benchmark" system is essentially exact. Most importantly, inelastic collision studies at this level of rigor have allowed us to identify quantitative discrepancies in the energy surfaces for almost all of the other scattering systems investigated, and thereby test the current reliability of potential surface extraction from both *ab initio* and empirical methods.

The sub-Doppler spectral resolution of the IR laser probe method also permits this scattering method to obtain angular velocity distributions of the final quantum levels, and thus differential scattering information with complete state-to-state labeling. We have developed high resolution IR laser Dopplerimetry methods based on singular value decomposition (SVD) algorithms, which extract $d\sigma/d\Omega$ on a finite grid of $\cos(\theta_{\text{com}})$ scattering angles, with $\Delta\theta_{\text{com}} \approx 6^\circ$

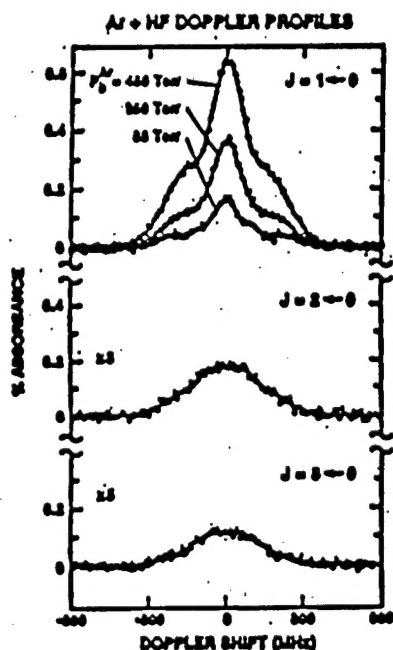


Fig. 4. Experimental $\text{Ar} + \text{HF}(J=0)$ Doppler profiles

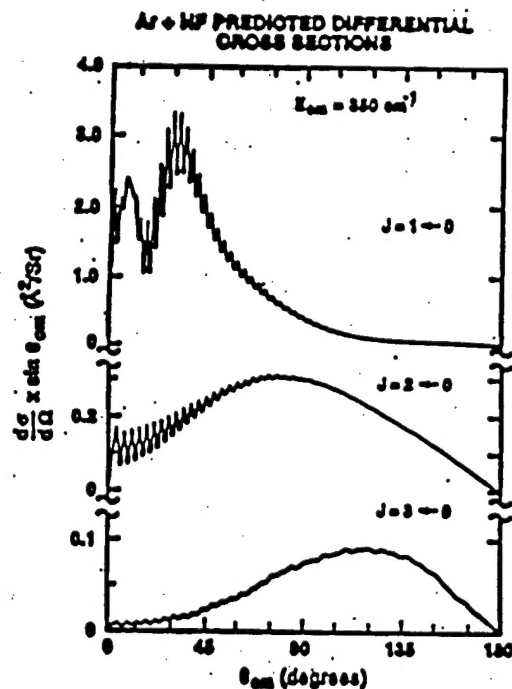


Fig. 5. Theoretical $\text{Ar} + \text{HF}(J=0)$ differential cross sections

and 25° angular resolution near 90° and 0° , respectively. Though not competitive with crossed beam methods, this angular resolution is already sufficient to resolve rotational rainbows in $d\sigma/d\Omega$, as well as angular structure due to quantum interference between open rotational channels. This is most clearly evident in the experimental Doppler profiles for Ar + HF($J=0$) scattering into $J=1,2$ and 3 (see Fig. 4), which demonstrate narrow "peak" and "pedestal" interference structures for $J=1 \leftarrow 0$ that correspond extremely well with the slow undulation in the forward vs. sideways scattering differential cross sections predicted from full QM calculations shown in Fig. 5.

B. High resolution pressure broadening studies of OH radicals

In modeling the IR "airglow" signatures, there is a need for rotational state dependent pressure broadening data for OH, which we have obtained in the limit of *thermal* OH($N \leq 4$) via high resolution flash kinetic spectroscopy. OH concentrations are produced by 193 nm photolysis of HNO_3 in flow mixtures, rapidly thermalized by collisions with buffer gas, and monitored by direct IR absorption with the single mode F-center laser. Lorentzian broadening contributions are extracted from a Voigt analysis, and used to extract pressure broadening rates for Ar, He, O_2 and N_2 collision partners (see sample data in Fig 6). The studies indicate a clear decrease in collisional broadening rates with rotational quantum number N , which is qualitatively consistent with slow relaxation of the high N states ($N \approx 33$) observed in the OH "airglow". Blumberg and coworkers have used these OH pressure broadening data to fit statistical energy gap law parameters and thereby extrapolate out to rotational relaxation values for the much higher N states; the results indicate an improved agreement with least squares modeling of the experimentally observed "airglow" distributions.

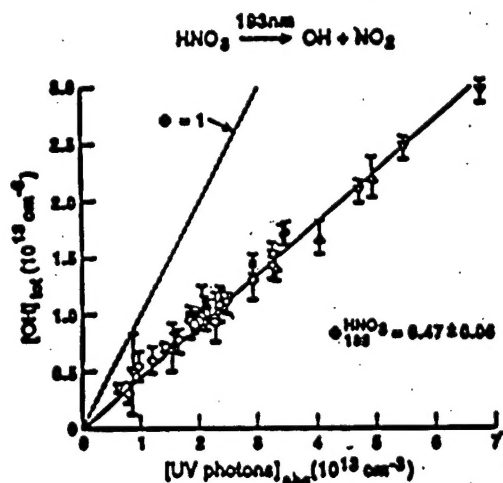


Fig. 6. Sample OH quantum yield data

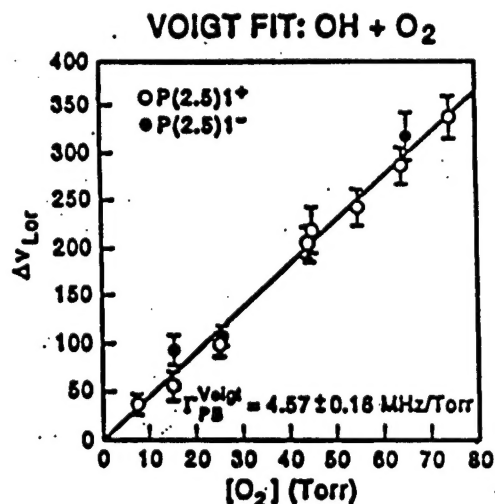


Fig. 7. Sample pressure broadening data for OH + O_2

C. Flash kinetic studies of absolute OH photolysis quantum yields

Photolysis quantum yields can be quite difficult to determine **absolutely**, as noted in recent jet measurements of HNO_3 by Butler and coworkers. However, one alternative is to use *direct absorption* methods to determine *absolute* concentrations of both i) absorbed UV photons and ii) photolysis radical product, which we have exploited to extract quantum yields for OH production from 193 and 248 nm photolysis of H_2O_2 and HNO_3 . Sample results for 193 nm photolysis of HNO_3 are shown in Fig. 7; the slope ($\Phi = 0.46(13)$) clearly identifies contributions from non $\text{O}_2\text{N-OH}$ bond breaking pathways not considered in atmospheric models. These results have been qualitatively corroborated by Ravishankara, Lee and Curl, who observe O, H and HONO products from competing $\text{HONO} + \text{O}$ and $\text{NO}_3 + \text{H}$ channels.

D. Radiative lifetime of the $\text{O}_2(^1\Delta_g) - \text{O}_2(^3\Sigma_g^-)$ "airglow" emission at 1.27 μm

One of the strong "airglow" features in the terrestrial mesosphere and lower thermosphere is due to molecular oxygen emitting on the $\text{O}_2(^1\Delta_g) \rightarrow \text{O}_2(^3\Sigma_g^-)$ band. This transition is highly forbidden ($\Delta\Sigma$, singlet-triplet, and g-g) and thus the Einstein A coefficient has only been "measured" indirectly by long path integrated absorption studies of the Einstein B coefficient. However, this conversion between A and B is somewhat complicated in O_2 due to change in spin multiplicity and the vanishing of alternate J levels due to nuclear spin statistics, which in the 30 years since the original grating spectrometer work of Badger has led to implicit (but unrealized!) 2-fold discrepancies in the literature. The correct method of analysis can be readily verified numerous ways; we simply rederived the Einstein relations for a state-resolved m_J manifold in equilibrium at a given T, and evaluated the "effective" degeneracy ratio in the appropriate high temperature (i.e. classical) limit. When applied to much more recent (and presumably more accurate) high resolution FTIR $\text{O}_2(^1\Delta_g)$ data, the revised analysis predicts an A value 75% *smaller* than the previous, lower resolution results of Badger et al. Since the Badger value is universally used to infer absolute $\text{O}_2(^1\Delta_g)$ concentrations, this result could have as much as a 1.75-fold influence on atmospheric "airglow" models from satellite data or chemical efficiency of the COIL laser system. Our work has stimulated efforts toward two new measurements of the $\text{O}_2(^1\Delta_g)$ radiative rate by Dr. John Ballard (Rutherford Appleton Laboratory) using Fourier Transform IR and Dr. Gordon Hager (Air Force Philips Lab) using cavity ringdown methods.

E. Inelastic and differential scattering with hyperthermal Cl atoms

Due to background IR generation in both exhaust plumes and low earth orbit environments, there is considerable interest in collision dynamics at **hyperthermal** velocities. As a simple test case, we have used 308 nm photolysis of Cl_2 to generate open shell $\text{Cl}(^2\text{P}_{3/2})$ radicals with lab frame velocities ≈ 2 km/sec, and thereby study state-resolved scattering of "hot" Cl atoms with room temperature HCl ($v=0, J_i \approx 3$) into $J_f=4,5,6\dots 12$. This system is of particular interest in work by Neumark and coworkers on photodetachment of $[\text{ClHCl}]^+$ to access the neutral transition state region, as well as efforts by Gordon and Schatz to generate accurate potential surfaces for reactive H atom exchange. HCl in a given final J_f state is monitored under

single collision conditions by direct absorption on $R(J_r)$ branch transitions of the $v=1 \leftarrow 0$ vibrational band, with the nascent velocity distributions probed by IR Dopplerimetry at 0.0001 cm^{-1} resolution. From the area of the 300K Gaussian "hole" written onto the HCl Doppler profiles at early time, one measures the absolute integral cross sections for hyperthermal collisional loss out of the initial J state. From the concomitant growth of the broader Doppler profile, one obtains absolute integral cross sections for collisional gain into the final J state. These studies reveal a rapid drop off in HCl states ($J \leq 12$) far below the energetic limit ($J_{\text{max}} \approx 18$), which is consistent with a simple classical picture of optimum rotational energy transfer for Cl collisions predominantly with the light H atom. This would also predict predominantly forward scattering of the Cl atom; this is supported by a differential scattering analysis from IR Dopplerimetry and in good agreement with theory (see Fig. 8). Interestingly, however, quasiclassical trajectory predictions on the Gordon and Schatz potential surface indicate a clear shift toward sideways and backward scattering at the highest J values which is not seen in the experimental data. These discrepancies at high J would suggest that the real potential surface has either a slightly higher barrier or tighter ClHCl bending coordinate in the transition state region.

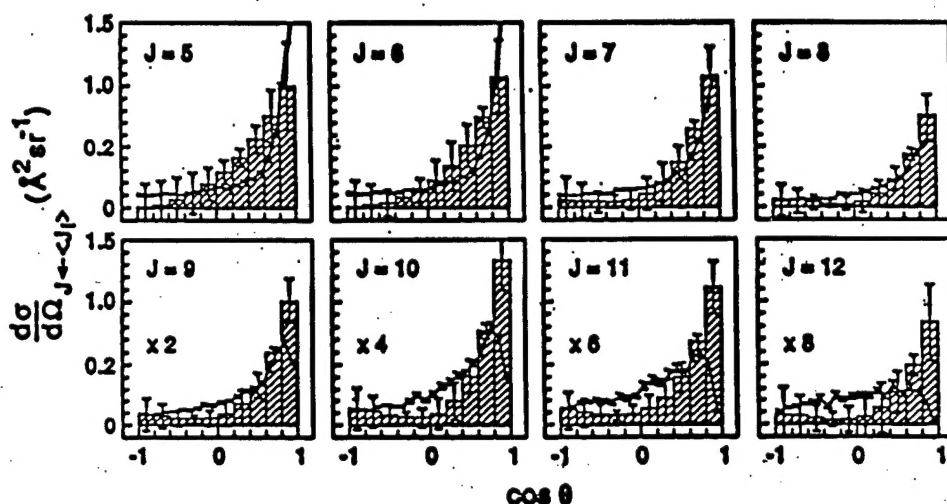


Fig. 8. State-resolved differential scattering of $\text{Cl} + \text{HCl}$ at $E_{\text{coll}} = 2000 \text{ cm}^{-1}$: expt (bar) and theory (line)

F. Rotational alignment from hyperthermal $\text{He} + \text{CO}_2$ collisions

Hyperthermal collision phenomena with directed velocity flow can lead to significant alignment of the rotational angular momentum. This effect can be particularly dramatic for linear molecules such as CO_2 seeded in a supersonic He expansion, due to high velocity slip collisions initially present in the expansion nozzle. To investigate these rotational alignment phenomena, we have developed a sub-Doppler probe method based on i) direct IR absorption of a tunable single mode diode laser and ii) rapid polarization switching with a photoelastic modulator (PEM). The tunable IR diode laser permits selection of individual rotational states and Doppler velocity

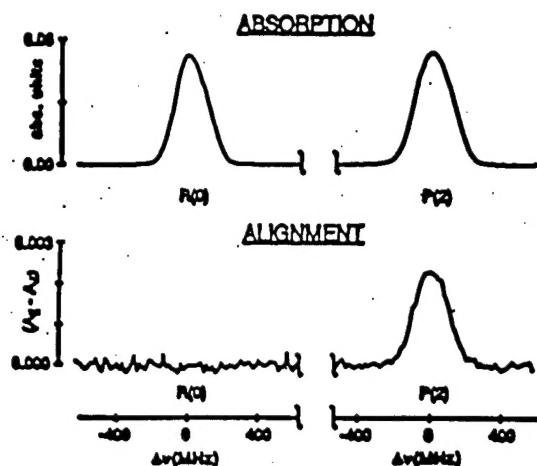


Fig. 9. Rotational alignment signals from He + CO₂

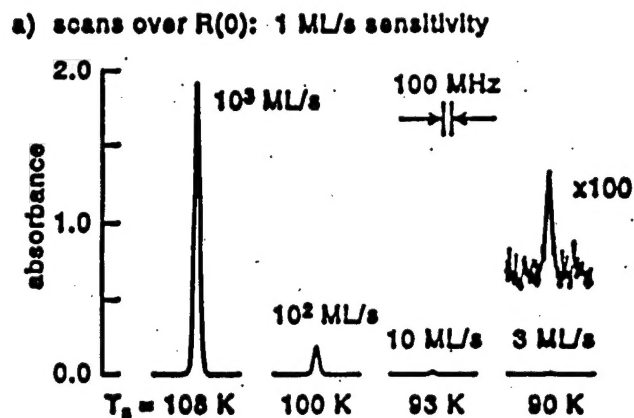


Fig. 10. Submonolayer/sec sensitivity for gas-surface CO₂ flux

projections, which can therefore elucidate the J state and transverse velocity dependence of the alignment dynamics. For the simplest case, Fig. 9 displays both absorbance and alignment signals for $J=0$ and $J=2$ rotational states from CO₂ + He collisions. As expected, $J=0$ shows no alignment, whereas the $J=2$ level shows significant **negative** alignment corresponding to an axis of rotation preferentially perpendicular to the expansion flow. This is consistent with the simple classical model of a linear rotor presenting a smaller m_J changing cross section for $|m_J| \approx 0$ ("cartwheel") rather than $|m_J| \approx J$ ("helicopter") collisions. The magnitude of this collisional alignment effect can be surprisingly large even under modest expansion conditions (≤ 1000 Torr), with up to 60% skewing of perpendicular vs. parallel projections of J .

G. State-resolved gas-surface collision dynamics on thin films

Collision dynamics at the gas-surface interface play an important role in hyperthermal accommodation coefficients in the shuttle environment. In a related direction, we have first investigated the quantum state resolved dynamics of gas-surface collisions at much lower collision energies. Specifically, IR laser based absorption methods have been used to probe the nascent quantum state distributions of molecules subliming from thin films; via microscopic reversibility, this permits a measure of absolute "sticking coefficients" as a function of rotational quantum state, alignment, vibrational state, velocity etc. These studies are performed by depositing 300 μm films of CO₂, varying surface temperatures, and probing the collision free flux via direct absorption of a single mode IR diode laser multipassed 1 cm above the surface. Fig. 10 demonstrates the high sensitivity of the IR method; one can readily probe single quantum states of CO₂ down to sublimation rates of < 1 monolayer/sec. The results indicate $S = 1.0 \pm 0.1$ for all quantum states observed up to $T_s = 110\text{K}$, which at our sensitivity corresponds to $E \leq 600\text{ cm}^{-1}$ collision energies.

Awards / Fellowships:

American Physical Society Fellow, 1991-present
Edward Uhler Condon Award, 1995
Silver Medal, Department of Commerce, 1995

Inventions or patent disclosures:

Cooperative research and development agreement (CRADA) with Hewlett-Packard to help develop H^{13}CN gas cells for situ calibration of optical spectrum analyzers

Publications resulting from AFOSR supported projects (1994-96):

- 1) D. J. Nesbitt, "Probing potential energy surfaces via high resolution IR laser spectroscopy," Faraday Discuss. Chem. Soc. 97, 1 (1994).
- 2) M. A. Suhm and D. J. Nesbitt, "Potential surfaces and dynamics of weakly bound trimers: Perspectives from high resolution IR spectroscopy," Chem. Soc. Reviews 24, 45 (1995).
- 3) Z.-Q. Zhao, W. B. Chapman and D. J. Nesbitt, "State-resolved rotational energy transfer in open shell collisions: $\text{Cl}(^2\text{P}_{3/2}) + \text{HCl}$," J. Chem. Phys. 102, 7046 (1995).
- 4) M. G. Mlynczak and D. J. Nesbitt, "The Einstein coefficient for spontaneous emission of the $\text{O}_2(a^1\Delta_g)$ State," Geophys. Res. Lett. 22, 1381 (1995).
- 5) Z.-Q. Zhao, W. B. Chapman and D. J. Nesbitt, "State-resolved rotational energy transfer in open shell collisions: $\text{Cl}(^2\text{P}_{3/2}) + \text{HCl}$," J. Chem. Phys. 102, 7046 (1995).
- 6) M. G. Mlynczak and D. J. Nesbitt, "The Einstein coefficient for spontaneous emission of the $\text{O}_2(a^1\Delta_g)$ State," Geophys. Res. Lett. 22, 1381 (1995).
- 7) Z.-Q. Zhao, W. B. Chapman and D. J. Nesbitt, "State-resolved differential scattering in open-shell collisions: $\text{Cl}(^2\text{P}_{3/2}) + \text{HCl}$ from high resolution IR laser Dopplerimetry," J. Chem. Phys. 104, 3555 (1996).
- 8) A. Schiffman, W. B. Chapman, J. M. Hutson and D. J. Nesbitt, "State-to-state rotational energy transfer dynamics in crossed supersonic jets: A high resolution IR absorption method," J. Phys. Chem. 100, 3402 (1996).
- 9) M. J. Weida, J. M. Sperhac and D. J. Nesbitt, "Sublimation dynamics of CO_2 thin films: A high resolution diode laser study of quantum state-resolved sticking coefficients," J. Chem. Phys. 105, 749 (1996).

10) W. B. Chapman, A. Schiffman and D. J. Nesbitt, "Rotationally inelastic scattering in $\text{CH}_4 + \text{He}$, Ne and Ar : State-to-state cross sections via infrared laser absorption spectroscopy in crossed jets," J. Chem. Phys. 105, 3497 (1996).

11) D. J. Nesbitt and R. W. Field, "Vibrational energy flow in highly excited molecules: Role of Intramolecular Vibrational Relaxation (IVR)," invited review for the 100th anniversary of J. Phys. Chem. 100, 12735 (1996).

12) D. T. Anderson, S. Davis, T. S. Zwier and D. J. Nesbitt, "An intense slit discharge source of jet cooled molecular ions and radicals", Chem. Phys. Lett. (in press)

13) W. B. Chapman, M. J. Weida and D. J. Nesbitt, "State-to-state scattering of $\text{HF} + \text{He}$, Ne and Ar : Cross sections, Dopplerimetry and alignment studies via direct IR laser absorption in crossed supersonic jets", J. Chem. Phys. (submitted)

Interactions/Transitions

Supervisory Committees:

Chair of 1996 Atomic and Molecular Interactions Gordon Conference
International Advisory Committee for Molecular Spectroscopy Symposium
Symposium organizer for 1997 spring meeting, American Chemical Society
Advisory committee for 1997 spring joint DCP/DAMOP meeting

Consultative/advisory functions to other laboratories:

1) Our AFOSR supported research results on the OH dipole moment function continue to be requested by other research groups and R&D companies. One example has been a request by Southwest Sciences, Inc. who are trying to develop in situ monitoring methods for detecting tropospheric OH radical using tunable diode lasers on the $v=2-0$ band in the 1.3-1.5 μm region. Another example has been the use of OH radiative lifetimes to model thermal 'de-NOx' processes, which is a commercially important process in smokestack pollution control.

2) Our reanalysis of the $\text{O}_2(^1\Delta)$ radiative lifetime has stimulated the initiation of several other measurements of this fundamentally important atmospheric system. Two examples are: Dr. John Ballard at the Appleton Research Laboratory in Cambridge, England has used long path length FTIR to record O_2 spectra in the 1.3 μm region at sufficient sensitivity and low enough pressure to eliminate side contribution from collision induced absorption effects. In addition, Drs. Harold Miller, Jim Dodd, and Gordon Hager at the Air Force Phillips Lab have recently developed a ring down cavity method for tunable absorption in the 1.3 μm region, and are applying this to an absolute band strength measurement of the $\text{O}_2(^1\Delta)-\text{O}_2(^3\Sigma)$ band.

3) I have provided consulting advice to Marlowe Engineering for developing ways to measure water vapor in high efficiency H_2/O_2 combustion systems.

4) I have been in consultation with researchers at NASA Goddard Space Flight Center, Laboratory for Atmospheres, Climate and Radiation Branch about enhanced IR absorption in clouds due to the presence of small water clusters. The presence of these enhanced absorption features is an outstanding problem in the modeling of global warming phenomena.

5) The slit discharge method we have recently developed for generating high densities of jet cooled radicals and molecular ions was written up in a weekly journal on technical innovation "Inside R&D" and "Physics World". This has resulted in several phone calls from industrial researchers interested in applications of these methods to chemical vapor deposition and plasma diagnostics.

Invited presentations of AFOSR research results:

1) "State-to-state dynamics and intermolecular potentials: insights from high resolution near-IR laser methods," University of California, Berkeley, CA, May 2, 1995.

2) "State-to-state dynamics and intermolecular potentials: insights from high resolution near-IR laser methods," California Institute of Technology, Pasadena, CA, May 16, 1995.

3) "IR-UV double resonance studies of photolysis in quantum state-selected clusters," Conference on the Dynamics of Molecular Collisions, Asilomar, CA, July 19, 1995.

4) "Probing intermolecular potentials and state-to-state dynamics: Full and half collision perspectives", 1995 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, December 21, 1995.

5) "Watching molecules touch: Intermolecular potentials and state-to-state dynamics via high resolution IR laser methods", Department of Chemistry, University of Pittsburgh, Pittsburgh, PA, February 8, 1996

6) "Watching molecules touch: Intermolecular potentials and state-to-state dynamics via high resolution IR laser methods", Department of Chemistry, Yale University, New Haven, CT, February 27, 1996.

7) "Hydrogen bonding, atmospheric radicals and nanocrystals: A high resolution IR perspective", Department of Chemistry, Harvard University, Cambridge, MA, March 13, 1996.

8) "State-to-state dynamics with high resolution IR lasers: Watching molecules touch", Department of Chemistry, University of Chicago, Chicago, IL, March 25, 1996.

9) "Hydrogen bonding, radicals and nanoclusters", Department of Chemistry, Texas Tech University, Lubbock, TX, April 3, 1996.

10) "Molecular spectroscopy and dynamics of transient species: A high resolution IR approach", Institute for Molecular Sciences, Okazaki, Japan, May 28, 1996.